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SPECTROSCOPIC ANALYSIS OF ELECTRICALLY POLARIZED POLY(ACRYLONIT--ETC(U)
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"SPECTROSCOPIC ANALYSIS OF ELECTRICALLY POLARIZED POLY(ACRYLONITRILE)"

by

S. I. Stupp and S. H. Carr

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Electrically polarized and unpolarized films of poly(acrylonitrile) have been investigated by both infrared attenuated total reflection (ATR) and thermally stimulated discharge (TSD). ATR analysis of PAN films has been aimed at explaining the molecular origin of thermally stimulated currents, and consequently that of phenomena contributing to electrical

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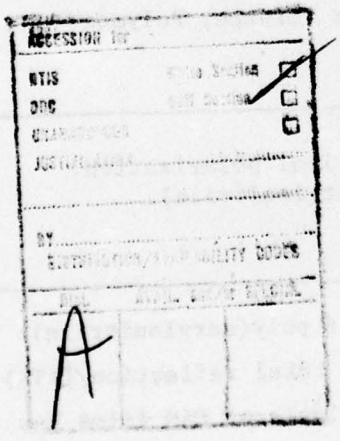
polarization in this material. Preferred orientation of nitrile dipoles along the thickness direction (applied electric field direction) has been detected by ATR in both polarized and unpolarized films. It is suggested that dipolar alignment in unpolarized solvent cast films results from internal electric fields associated with space charges. The observed orientational anisotropy is found to disappear gradually as films (both polarized and unpolarized) are heated from ambient temperature to 100°C and rotational motion in the backbone is thermally activated. TSD currents observed in this thermal range are thus associated with randomization of molecular dipoles. TSD currents observed above 100°C are suggested to originate from drift of space charges, since both an isotropic orientation of dipoles and onset of considerable diffusion are detected by ATR in this temperature range. PAN films polarized by high-intensity electric fields (5×10^5 Vcm^{-1}, as opposed to 5×10^4 Vcm^{-1}) are found to retain orientational anisotropy above 100°C, and this is believed to be associated with a structural rearrangement induced by electrical polarization.



"SPECTROSCOPIC ANALYSIS OF ELECTRICALLY POLARIZED POLY(ACRYLONITRILE)"

INTRODUCTION

The ability of polymer solids to retain electrical polarization for long times at low temperatures has been recognized experimentally over the past few decades (1-6). Experimental techniques that thermally scan depolarization currents have been used in the past to estimate the magnitude of polarization and to obtain information related to molecular origin of polarization (7-11). An example is thermally stimulated discharge (TSD), which has been described in detail elsewhere (12). Electrical polarization in polymers can be due to several molecular phenomena. One possibility is the alignment of molecular dipoles along a preferred direction. This requires conformational rearrangements and can only be induced by an electrical driving force at temperatures where relaxation times for such molecular motions are short. These dipolar alignments, once induced at high temperatures, are retained in the absence of an electrical potential at lower temperatures where relaxation times are very long. Other contributions to electrical polarization might result from drift of ionic impurities toward electrodes of charge opposite to that of these individual ions. These contributions can also be retained at low temperatures due to greatly diminished diffusion coefficients.

The present investigation has been aimed at introducing the use of infrared internal reflection spectroscopy (ATR) (13) as a means of characterizing electrical polarization in polymers. The rationale for use of ATR, as opposed to conventional transmission infrared, is the possibility of measuring relative absorption coefficients in each of the three orthogonal directions

of the sample (13), thus allowing more complete characterization of dipola orientation. Such measurements are possible by ATR due to the fact that radiation at the interface between reflecting crystal and polymer specimen contains electric fields which project some component onto each of these three coordinate directions of the sample (14,15). In the present investigation, spectroscopic analysis has been carried out as samples were being thermally depolarized and, as a result, these experiments make it possible to resolve that contribution to electrical polarization from oriented dipoles. On the other hand, this isolation is difficult in some cases by techniques such as TSD since molecular motion and diffusion of small chemical species are often activated in overlapping temperature ranges. An additional advantage of ATR for the present investigation is the fact that only the first few thousands of Angstroms below the specimen surface are spectroscopically analyzed, and it is therefore possible to detect surface effects contributing to electrical polarization, as well. For example, it might be that preferred orientation of dipoles is more pronounced in surface layers of the material, yet if one were analyzing the entire film by transmission, such surface effects would be hardly detectable experimentally on the bulk average basis.

Poly(acrylonitrile) (PAN) has been the material selected for the present investigation. PAN dielectrics have been found to store a substantial amount of electrical polarization, as has been concluded from previous TSD (16-18) work on both externally polarized and unpolarized films. Several molecular phenomena are expected to contribute to polarization in this material, since dipolar alignment alone cannot account for total observed polarization (18). Two examples are: trapped space charges, which result from asymmetric displacement of ionic impurities (18), and a concentration gradient across the film's thickness of ionic species, which can be generated as a consequence

of chemical degradation above 180°C (19). Nevertheless, an electric field would be expected to induce conformational rearrangements and thus orientation of dipoles to a considerable extent, due to the strong dipole moment of nitrile side groups (3.4 Debye units) and the limited structural order in the PAN solid state (20-22). Limited order implies molecular organization whose character possesses two dimensional order (lateral spacing between chains) but which lacks fully developed crystallinity. In the present work, the extent of molecular rearrangement induced by electric fields in PAN and resulting dipolar orientation have been investigated by both TSD and ATR spectroscopic analysis.

EXPERIMENTAL

Poly(acrylonitrile) films were cast on glass surfaces from 2% solutions in dimethyl formamide. Evaporation of solvent was accomplished by exposing solutions to vacuum at room temperature for 24 hours. Films obtained by this procedure were subsequently cut into segments whose thickness ranged from 15 to 35 microns. Samples were placed loosely between glass plates and exposed to vacuum at $40^{o}C$ for 24 hours in an effort to reduce further the content of DMF. PAN films doped with NH_4NO_3 were prepared by dissolving the salt in DMF and subsequently adding it dropwise to PAN solutions in DMF. The PAN used in these experiments was a custom-made batch of homopolymer that was supplied to us courtesy of the Vistron Corporation, Cleveland, Ohio. Gold electrodes were vacuum-deposited on opposite surfaces of the samples.

Samples were polarized in a device constructed in these laboratories. The apparatus includes a Hewlett-Packard model 6525A DC voltage source, a Data-Trak Model 5310 programmed temperature controller coupled to a Phaser Model 632 power supply, and a Leeds and Northrup dual channel strip-chart recorder. Specimens in the sample chamber were clamped at opposite ends, and contact with the electrodes was made with silver cement. Prior to spectroscopic analysis, gold electrodes evaporated on the samples were removed by rubbing gently with a cotton swab that was wet with methanol. This procedure was investigated thoroughly for its potential of introducing artifactual information and was found not to have any effect on experimental data obtained. TSD spectra were recorded with the "Electret Thermal Analyzer", manufactured by Toyo Seiki Seisaku-Sho, Ltd. and distributed in U.S.A. by Atlas Electric Devices Co., Chicago, Illinois 60613.

The infrared spectrophotometer used was a Perkin Elmer Model 180, fitted

with a twin-parallel-mirror reflection attachment (TPRMA) from Harrick Scientific Corporation, Ossining, New York 10562. Transmittance measurements obtained with this instrument were accurate to ±0.4%. The internal reflection plate used was a parallelepiped zinc selenide crystal (θ=45^{o}). Contact between the internal reflection element and the sample was accomplished using pressure plates and a torque-limiting screw driver. The pressure plates were equipped with heating cartridges connected to a Variac power source and a thermocouple connected to a digital thermometer. Temperature measurements were accurate to ±1^{o} in the reported experiments.

RESULTS

As was previously pointed out, it is possible by ATR to measure absorption components along three orthogonal directions of a sample. In the present work, components along three Cartesian coordinates were measured for the nitrile group absorption coefficient (k_x, k_y, k_z). The vibrational mode corresponding to stretching of the nitrile dipole in PAN gives rise to a sharp infrared absorption maximum at approximately 2240 cm^{-1}. This absorption band, used for all spectroscopic analysis in the present work, is well isolated from other peaks in the infrared spectrum of PAN. At the same time, the nitrile stretching vibration is uncoupled with other modes owing to the large force constant associated with the carbon-nitrogen triple bond. Measurement of directional components can be done by combining reflectivity measurements with light having perpendicular and parallel polarization. The following relations were derived by Fluornoy and Schaffers (14,15) starting out with Maxwell field equations and Fresnel's equation:

$$\ln R_{\perp} = - \frac{4n_2^2 k_x}{n_1^2 \tan\theta \left(1 - \frac{n_2^2}{n_1^2 \sin^2\theta}\right)^{1/2} \left(1 - \frac{n_2^2}{n_1^2}\right)}$$

$$\ln R_{\parallel} = - \frac{4n_2^2 \left[kz + 1 - \frac{n_2^2}{n_1^2 \sin^2\theta} ky\right]}{n_1^2 \tan\theta \left(1 - \frac{n_2^2}{n_1^2 \sin^2\theta}\right)^{1/2} \left(1 - \frac{n_2^2}{n_1^2 \sin^2\theta} + \frac{n_2^4 \cot^2\theta}{n_1^4}\right)}$$

where,

R = reflectivity

θ = angle of incidence

n_1 = refractive index of reflecting crystal

n_2 = refractive index of the sample.

The relative magnitudes of different spatial components were measured through the following parameters: $\frac{k_x}{k_x+k_y+k_z}$, $\frac{k_y}{k_x+k_y+k_z}$ (planar components) and $\frac{k_z}{k_x+k_y+k_z}$ (thickness component). Planar components were measured by rotating films 90° around the z-axis. These parameters were measured for an unpolarized film of PAN as a function of temperature as shown in Figs. 1b,1c. Only one of the planar components is shown since both were found to be identical. Interestingly, slight anisotropy in nitrile dipole orientation is observed in the unpolarized film with preferred orientation along the thickness direction. Such preferred orientation is lost with increasing temperature in the thermal range between 60 and 100°C. Above 100°C all components reach a relative magnitude of 0.33 indicating spatial randomization of dipoles.

TSD and ATR analysis of samples never exposed to a thermoelectric schedule suggest lack of electrical neutrality in these films. Fig. 1a shows the TSD spectrum of an unpolarized PAN film between room temperature and 200°C. One notes the existence of a depolarization current maximum and loss of preferred orientation of dipoles, as detected by ATR, in the same temperature range, suggesting a correlation between both experimental observations. Current maxima of opposite polarity and of higher intensity (approximately by a factor of 500) are observed above 100°C. Spectroscopic analysis indicates isotropy in dipole orientation above 100°C, and thus it may be inferred that the molecular origin of these currents is most probably not dipolar.

Currents above 100°C in unpolarized films are most likely associated with trapped space charges, and thus with thermally activated diffusion of

small chemical species. Experimental support for this suggestion was obtained by conducting additional ATR experiments, in which the thermal dependence of diffusion was analyzed. The ionic compound NH_4NO_3 was deliberately introduced in PAN films (10% by weight) and experiments carried out in which diffusion of NO_3^- ions was analyzed. A concentration gradient of NH_4NO_3 develops across the thickness of films during film casting, with the surface contacting the substrate containing the excess of NH_4NO_3. Diffusion of NO_3^- ions across this gradient was then analyzed by following relative changes in concentration of NO_3^- ions as a function of temperature. This was carried out by measuring absorbance near 830 cm^{-1}, (normalized by an internal standard band) associated with the nitrate ion (23). Similar experiments were carried out with the purpose of analyzing diffusion of residual solvent through the films. In this case, relative changes in concentration with increasing temperature were followed by measuring absorbance of the carbonyl band from DMF (1660 cm^{-1}). Results obtained from these experiments are shown in Figs. 2b,2c, and it can be seen that diffusion of small chemical species becomes substantial in the temperature range coincident with intense TSD currents. This observation is thus suggestive of a single origin of the two phenomena.

Prior to analyzing externally polarized samples, it is necessary to investigate any effects caused by annealing alone. Table 1 shows the effect of annealing on orientational anisotropy. The thermal history used in annealing samples was identical to that used when polarizing samples by an external potential. At ambient temperature, anisotropy along the thickness direction is observed as indicated in data described above. The sample is then heated at 2^oC/min to the temperature at which the external electric field would be applied (150^oC) if the sample were to be polarized. At this temperature, dipoles are assumed to be randomly oriented, and isotropy is preserved as the sample is annealed at constant temperature for 30 minutes,

as well as subsequent cooling to ambient temperature.

Spectroscopic analysis of PAN films exposed to external electrical potentials indicates that dipolar orientation is induced by electric fields. Figs. 3b,3c show the relative magnitudes of absorption coefficients as a function of temperature for a sample previously polarized by an external potential of 5×10^4 Vcm^{-1} at 130°C. Preferred orientation of dipoles along the applied field direction is evidenced by the observed increase in k_z (component along the electric field direction) at 32°C in the polarized sample relative to that in a sample annealed but not polarized (Table I). As indicated in Figs. 3b,3c randomization of oriented dipoles is thermally induced as the temperature is raised to 100°C. Fig. 3a is a TSD spectrum of a sample subjected to an identical thermoelectric schedule, showing a current maximum at ~90°C and again suggesting a correlation between the electrical and spectroscopic experiments. At the same time, TSD currents above 100°C of greater intensity than those in the unpolarized sample are observed in a temperature range where dipolar orientation is isotropic. Thus, even though these currents seem to result from electrical polarization, their origin is not dipolar. Similar spectroscopic analysis of PAN films polarized by high-intensity fields (5×10^5 Vcm^{-1}) reveals an interesting feature. As indicated in Figs. 4b,4c, anisotropy in dipole orientation in these samples is retained to higher temperatures (140°C, as opposed to 100°C in the case of polarization by a low-intensity field). Correspondingly, this feature revealed by spectroscopic analysis is consistent with TSD data (Fig. 4a), since no current flow is detected below 100°C.

Discussion

Anisotropy in dipole orientation in PAN as a function of temperature was the primary variable measured in the present investigation, and results are interpreted with the purpose of elucidating the molecular origin of electrical polarization. Measurement of this variable is also aimed at detection of any structural changes resulting as a consequence of electrical anisotropy in the material. Interpretation of the data obtained requires understanding of a basic concept, namely, that depolarization involves a transition from one state in which side group dipoles possess a biased orientation in space to one in which all dipoles are randomly oriented, and that this transition requires conformational rearrangements in the backbone (at least on a localized level). Consequently, the temperature at which loss of orientational anisotropy is detected by ATR can be considered as the onset of substantial backbone mobility (at least localized over very short segments, e.g., two or three backbone atoms). Moreover, changes in orientational anisotropy should occur in temperature ranges where dipolar TSD currents are observed. Since anisotropy loss during heating essentially traces the thermal dependence of molecular mobility in the structure, then any drastic thermal shifts resulting from changes in structure ought to be, in principle at least, observable by measurements carried out in this present investigation.

It is important to interpret data obtained with due care because antiparallel dispositions of dipoles along a given direction in space cannot be distinguished by infrared measurements. Specifically, a larger absorption coefficient along a given coordinate does not necessarily imply a net electrical polarization parallel to that direction, since dipoles, even though oriented along a preferred direction, might be randomly aligned in the parallel or antiparallel sense. Nevertheless, if chains were randomly oriented in a

polymeric film, it would be unlikely for dipole moments associated with side groups to develop a preferred orientation spontaneously, unless, of course, an electrical driving force, internal or external to the material, is involved. However, if this were the case, preferred orientation along a given Cartesian coordinate would imply that electric moments share the same spatial sense. In the present analysis of experimental results, it is assumed that equal relative absorption coefficients for nitrile dipoles along the three Cartesian coordinates previously defined $\left(\frac{k_x}{k_x+k_y+k_z} = \frac{k_y}{k_x+k_y+k_z} = \frac{k_z}{k_x+k_y+k_z} = 0.33\right)$ correspond to a state of random dipolar orientation and thus a state of zero net electrical polarization due to dipoles. On the other hand, a net electrical polarization can be preserved by the material even though relative absorption coefficients in three spatial directions become photometrically equal at a given temperature. However, this is not considered to be the case on the basis that a change from an anisotropic to an isotropic state of dipolar orientation (as detected spectroscopically) requires rotations around carbon-carbon bonds.

On the basis of previously presented arguments, it is proposed that a larger absorption coefficient along the thickness direction of never-polarized and unoriented PAN films indicates the existence of electrical anisotropy in solvent cast material. This proposal is supported further by the presence of a TSD current maximum in the same temperature range in which dipolar anisotropy is found to disappear. Furthermore, the progressive equalization of all three absorption coefficients with increasing temperature is indicative of some molecular motion in the material. This is based on the fact that loss of dipolar anisotropy can only occur when thermal energy activates bond rotations in the backbone. In fact, mechanically active and dielectric loss transitions in PAN have been previously observed in the temperature

range where dipolar anisotropy is lost (24-28). All investigators find a transition, which, depending on experimental conditions (and possibly on the source of the specific PAN analyzed), will occur in the range from 70°C to 110°C, which is the temperature range in which dipolar anisotropy is lost. Even though the origin of this transition has not been uniquely determined, Hayakawa, et al. (25) suggested that the transition observed at 85°C is associated with rotational vibration in the paracrystalline phase of PAN. In contrast to this suggestion, Meredith, et al. (24) associated a transition at 70°C with segmental rotation of chains in amorphous regions. Unfortunately, many details of the solid state structure of PAN remain unresolved (21) and molecular characterization of observed transitions is not possible. The fact that no drastic drop in elastic modulus is associated with any of the observed transitions (29) makes it inappropriate to associate mechanical and dielectric loss phenomena in PAN to an ordinary glass transition. Nevertheless, previous work on relaxation phenomena indicates the occurrence of some molecular motion starting near 70°C. Activation energy values obtained from TSD data generally agree with those reported earlier. For relaxation phenomena, however, analysis of these results will be deferred to a subsequent publication. The fact that loss of anisotropy is observed below 100°C in present experiments supports previous suggestions that rotational vibrations are associated with molecular mobility in this temperature range. Most importantly, it points out how this kind of ATR experiment can be used to characterize molecular motion in polymer solids.

As previously discussed, the existence of a net electrical polarization in the material due to dipolar alignment implies the involvement of an electrical driving force as the source of anisotropy. Since such dipolar anisotropy is found to occur in films never-polarized by external potentials,

one is lead to suggest that an internal electric field may be responsible for dipolar anisotropy in DMF solution-cast films of the specific PAN used. It is proposed that this internal electric field is possibly associated with space charges formed during solidification of PAN films by DMF solvent evaporation. The chemical species participating in formation of a space charge are thought to be ionic impurities introduced during polymerization of the monomer and handling of the material. Experimental evidence for the presence of such space charges is contained in the TSD spectrum of unpolarized solvent cast films. Specifically, the presence of strong current maxima above $100^{o}C$, which can be seen in Fig. 1a, is suggestive of an asymmetric surface charge distribution in the material. Integration of TSD current peaks yields, to a certain extent, the amount of charge stored in the material depending on the efficiency of the active decay processes (12). Inefficiency in measurement of stored polarization can be caused by recombination of image charges (which give rise to the measured discharge current) with charges near the surface.

On the other hand, TSD currents arising from randomization of oriented dipoles should be 100% efficient in measuring their contribution to persistent polarization (12). Thus, the total charge released, Q, is given by,

$$Q = \int_{o}^{\infty} J(t)dt$$

where J(t) is the TSD current from an experiment in which time, t, is proportional to temperature, T. Integrating both TSD current maxima above $100^{o}C$ ($135^{o}C$ and $190^{o}C$), and dividing by the electrode area ($1.5\ cm^{2}$) yields a value for $Q = 2.1 \times 10^{1}\ \mu C/cm^{2}$. The experimental value of Q, regardless of the molecular origin of these peaks, is less than the actual charge stored due to possible inefficiency in measurement as explained earlier (providing the maxima above $100^{o}C$ are not of dipolar origin) and also the fact that two

peaks are superimposed. An estimated upper bound value of $4.3\ \mu C/cm^2$ for polarization that could be due to oriented nitrile groups in PAN was reported earlier (18). However, the experimental value of polarization discharged above $100^{\circ}C$ exceeds that predicted for the case in which 100% of the nitrile dipoles acquire a preferred orientation. This observation suggests that currents above $100^{\circ}C$ are not of dipolar origin. Furthermore, ATR data indicate that complete randomization of nitrile dipoles occurs above this temperature. Instead, these currents are possibly associated with disappearance of a space charge which, in turn, is the origin of the internal electric field that biases dipoles into a preferred orientation in solvent cast film. Interestingly, the low temperature TSD current maximum is of opposite polarity to the high temperature maxima. This would be expected if whatever discharges above $100^{\circ}C$ were the source of the internal field giving rise to preferred orientation of dipoles.

At the present time, it is only possible to speculate on the molecular origin of polarization which decays above $100^{\circ}C$ in unpolarized films. Evidence has been obtained in the present investigation that supports the association of these currents with diffusion of ionic species and thus the possibility of a space charge. As shown in Fig. 2b,2c, diffusion of small molecules such as DMF (residual solvent) and NO_3 ions deliberately introduced in PAN films is significantly activated above $100^{\circ}C$. In a previous investigation (30), diffusion of perchlorate ions in a PAN matrix was also reported to be thermally activated above $100^{\circ}C$. As reported earlier (19), PAN films cast from DMF solutions under present conditions possess a solvent gradient between opposite surfaces, since solvent evaporation takes place more readily on the surface exposed to vacuum than on the one containing the casting substrate. Such solvent gradients could possibly act as precursors of an asymmetric displacement of ionic impurities between the top and bottom

surfaces of a film. For example, this could result if solvent (DMF in the present case) would preferentially bind ionic impurities of a given charge sign, thus creating a concentration gradient throughout the thickness during evaporation.

Both TSD and ATR analysis of films exposed to external potentials reveal acquisition of persistent electrical polarization. Since externally polarized films are exposed to electric fields at high temperatures ($130^{o}C$-$160^{o}C$), it is then necessary to examine any effects which annealing might have on these films. As expected, annealing of PAN films to $130^{o}C$ and above randomizes any dipolar anisotropy frozen-in during the casting procedure. Table 1 shows the changes undergone by films annealed to typical polarization temperatures and kept at these temperatures for 30 minutes, thus simulating the thermal schedule used during external polarization. Nevertheless, applying an electric field of 5×10^{4} Vcm^{-1} to PAN films at $130^{o}C$ induces preferred alignment of dipoles along the electric field direction (thickness direction of films). This is indicated by data shown in Fig. 3b. Dipolar anisotropy along the electric field direction is shown to decay as films are thermally stimulated, and at $100^{o}C$ randomization of dipoles is revealed by spectroscopic analysis. Also shown in Fig. 3a is a TSD current maximum occurring in the thermal range where absorption coefficients for the nitrile group progressively acquire equal values. This observation suggests a dipolar origin for the low temperature TSD current maximum in polarized PAN films. The percent of nitrile dipoles oriented along the electric field direction can be estimated from the relative magnitudes of absorption coefficients. To a first approximation this value is equal to ~10% for external polarization by a field of 5×10^{4} Vcm^{-1}. This is in reasonable agreement with the value obtained by integrating the area under the low temperature current maximum in a TSD spectrum (14%). This value is obtained assuming the dipole moment

of the nitrile group to be 3.4 Debye units and the number of nitrile groups per unit volume to be 1.3×10^{22} dipoles/cm^3 (based on density measurements and crystallographic information on the paracrystalline unit cell of PAN). Considering that prior to the application of the field at 130°C complete randomization is attained, the external potential induces a considerable degree of dipolar alignment. TSD currents above 100°C are too strong to be associated with randomization of oriented dipoles. Furthermore, there is no indication of dipolar anisotropy above 110°C from the ATR data. The high temperature maximum (~190°C) is believed to be associated with space charges and has been discussed in a previous publication (18). Similar calculations for the unpolarized films from both TSD and ATR data previously discussed yield values of ~1.5% and ~3.5% respectively.

The Langevin function for freely rotating dipoles,

$$P = \frac{N\mu^2 E_p}{3kT_p}$$

where P = polarization

μ = the dipole moment

k = Boltzmann's constant

E_p and T_p = polarization field and temperature,

predicts values for total polarization contributed by dipoles which are lower than those obtained experimentally (see Table 2). A possible source of discrepancies between calculated and observed degrees of orientation is the presence of strong internal fields in the condensed phase of the material. Localized field effects would be specially important in PAN solids owing to the strong dipole moment of the nitrile group and to their proximity to neighboring dipoles along the backbone (~3Å). Another possible source of discrepancies between calculated and observed degrees of orientation is a larger effective dipole moment for the nitrile group in solid PAN, greater than 3.4 Debye units (this value is obtained experimentally for small nitrile-

containing organic molecules in the gas phase). A larger value for the electric moment of the nitrile group could result from dipole-dipole interactions in the solid state.

As shown in Fig. 4a, polarization of a PAN film by a field of 5×10^5 Vcm^{-1}, as opposed to 5×10^4 Vcm^{-1} for the case previously discussed, modifies its TSD spectrum, and this is possibly associated with a chain backbone rearrangement induced by the strong electric field. Specifically, the modification observed is the disappearance of the low temperature TSD current maximum near 90^oC, which is proposed to be associated with randomization of dipoles. ATR data shown in Fig. 4b,4c reveals the presence of dipolar anisotropy to a higher degree than in films polarized at 5×10^4 Vcm^{-1}. At the same time, loss of anisotropy is observed by ATR at the onset of current flow in the TSD spectrum. Thus, one might suggest that the onset of substantial molecular mobility (e.g., rotational vibrations) has been shifted to higher temperatures thus hindering discharge of the dipolar contribution to polarization below 100^oC. The nature of a possible structural rearrangement as a consequence of electrical polarization would only be speculative at this point. Nonetheless, one might suggest the possibility that a higher degree of intermolecular bonding results as a consequence of a given percent of the dipoles acquiring a common orientation in space. An example would be an increase in the number of quadrupoles resulting from bonding between two dipoles sharing a common orientation in space but whose electric moments have aligned in antiparallel directions. At this point, it is only reasonable to propose that a thermal shift has occurred for the onset of substantial molecular mobility. However, the origin of this effect is not presently well understood, and the nature of a possible rearrangement in physical structure under the influence of intense electric fields is under investigation in our laboratories.

CONCLUSIONS

ATR spectroscopic analysis of electrically polarized films of PAN reveal preferred orientation of nitrile side groups along the electric field direction. This preferred orientation is found to disappear in temperature ranges where depolarization currents are observed by the TSD technique ($23^{o}C$-$140^{o}C$). The molecular origin of TSD currents above this temperature range is thus concluded to be ionic (motion of space charges) rather than dipolar. In agreement with TSD results, ATR analysis reveals preferred orientation of dipoles in unpolarized films of PAN. This dipolar anisotropy is believed to be associated with internal electric fields, which result from asymmetric displacement of ionic impurities in solvent-cast films.

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TABLE I

NITRILE ANISOTROPY OBSERVED UPON HEATING, ANNEALING[a], AND COOLING

Temperature	$\left(\frac{k_x}{k_x+k_y+k_z}\right)=\left(\frac{k_y}{k_x+k_y+k_z}\right)$	$\left(\frac{k_z}{k_x+k_y+k_z}\right)$
32°C	0.320	0.360
↓ heat[b]		
148°C (3 min.)	0.333	0.334
↓ hold		
148°C (10 min.)	0.344	0.313
↓ hold		
148°C (30 min.)	0.339	0.323
↓ cool[c]		
32°C	0.338	0.324

a. Note that 148°C is in the middle of the range of temperatures used for polarization treatments.
b. Heating rate: 2°C/min.
c. Regulated to duplicate TSD experiment.

TABLE II

EXPERIMENTAL AND CALCULATED VALUES FOR POLARIZATION

DUE TO DIPOLES IN POLY(ACRYLONITRILE)

Electric Field	ATR[a]	TSD[b,c]	Langevin equation[c]
0	3.5%±2.5%	1-2%	--------
5×10^4 Vcm^{-1}	$10.1\%^{+4.3\%}_{-6.5\%}$	11-17%	0.10%
5×10^5 Vcm^{-1}	12.5%±3%	------	1%

a. Estimated assuming $\left(\frac{k_i}{k_x+k_y+k_z}\right)_{i=x,y,z} = 0.33$ and $\left(\frac{k_z}{k_x+k_y+k_z}\right) = 1.00$ represent 0% and 100% orientation of dipoles, respectively.

b. Estimated from areas under TSD peaks.

c. Values calculated as per cent of maximum polarization (4.3 $\mu C/cm^2$).

FIGURE CAPTIONS

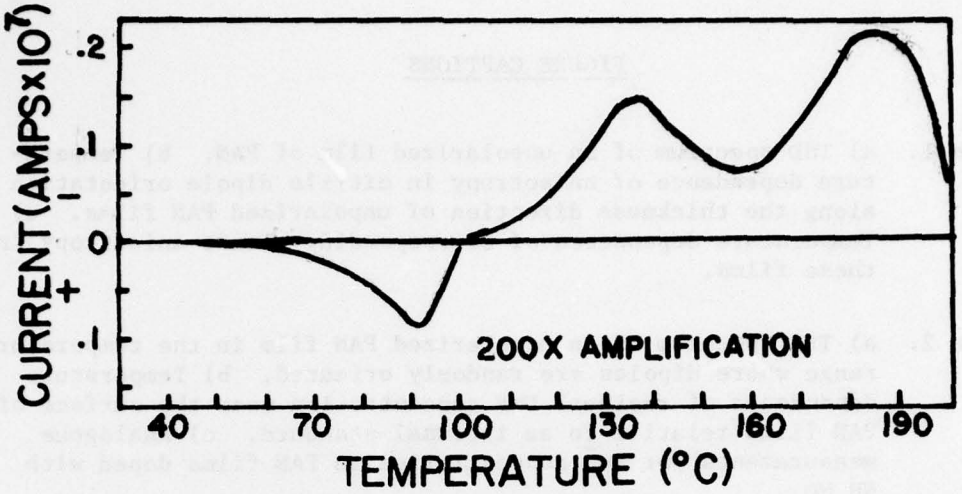
Figure 1. a) TSD spectrum of an unpolarized film of PAN. b) Temperature dependence of anisotropy in nitrile dipole orientation along the thickness direction of unpolarized PAN films. c) Temperature dependence of corresponding planar anisotropy in these films.

Figure 2. a) TSD spectrum of an unpolarized PAN film in the temperature range where dipoles are randomly oriented. b) Temperature dependence of residual DMF concentration near the surface of PAN films relative to an internal standard. c) Analogous measurements for NO_3^- concentration in PAN films doped with NH_4NO_3.

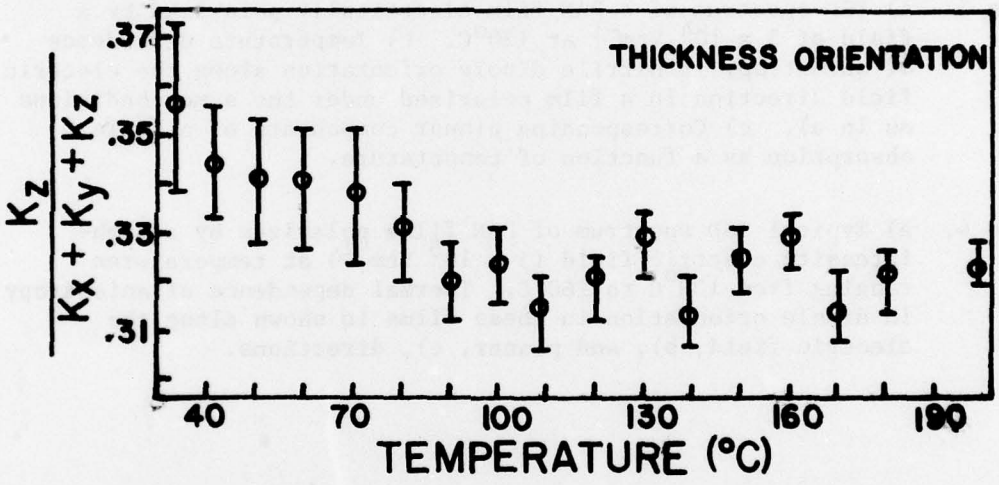
Figure 3. a) TSD spectrum of a PAN film electrically polarized by a field of 5×10^4 Vcm^{-1} at 130°C. b) Temperature dependence of anisotropy in nitrile dipole orientation along the electric field direction in a film polarized under the same conditions as in a). c) Corresponding planar components of nitrile absorption as a function of temperature.

Figure 4. a) Typical TSD spectrum of PAN films polarized by a high-intensity electric field (5×10^5 Vcm^{-1}) at temperatures ranging from 130°C to 160°C. Thermal dependence of anisotropy in dipole orientation in these films is shown along the electric field, b), and planar, c), directions.

a)


CURRENT (AMPS x 10⁷)
.2
.1
0
.1
+
-
200X AMPLIFICATION
40
70
100
130
160
190
TEMPERATURE (°C)

b)


Kz / Kx + Ky + Kz
.37
.35
.33
.31
THICKNESS ORIENTATION
40
70
100
130
160
190
TEMPERATURE (°C)

c)

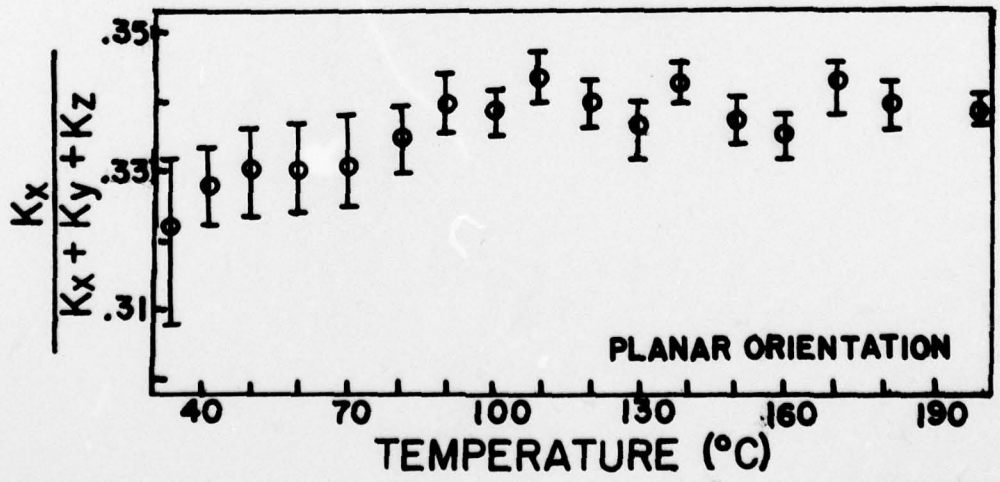
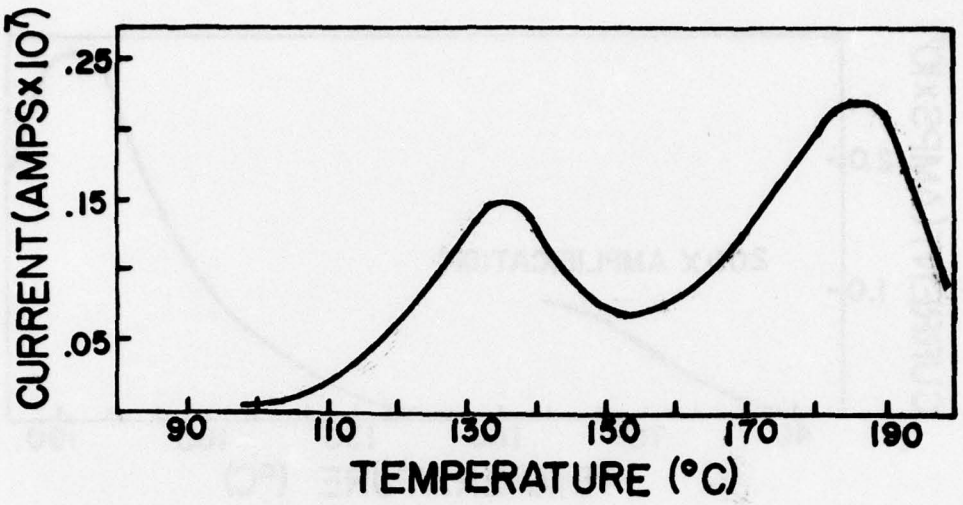
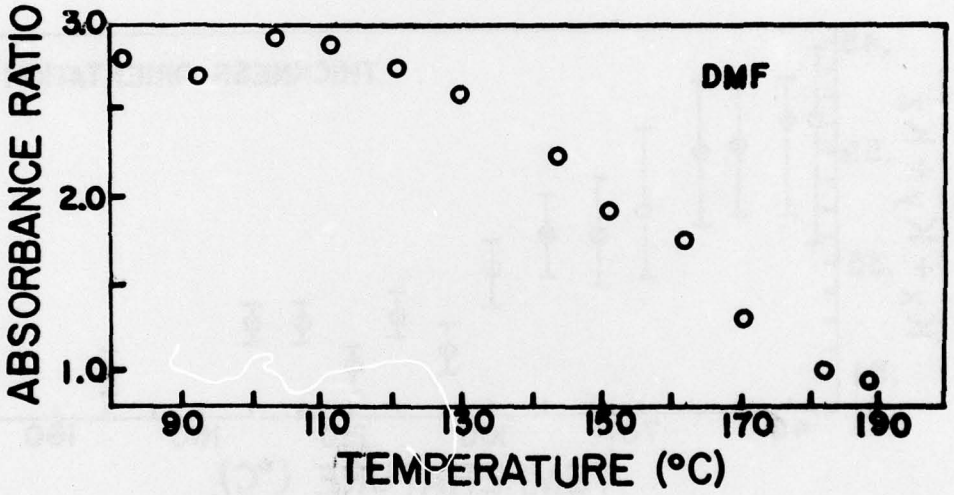

Kx / Kx + Ky + Kz
.35
.33
.31
PLANAR ORIENTATION
40
70
100
130
160
190
TEMPERATURE (°C)

Fig. 1 a,b,c

a)


CURRENT (AMPS x 10⁷)
.25
.15
.05
90
110
130
150
170
190
TEMPERATURE (°C)

b)


ABSORBANCE RATIO
3.0
2.0
1.0
DMF
90
110
130
150
170
190
TEMPERATURE (°C)

c)

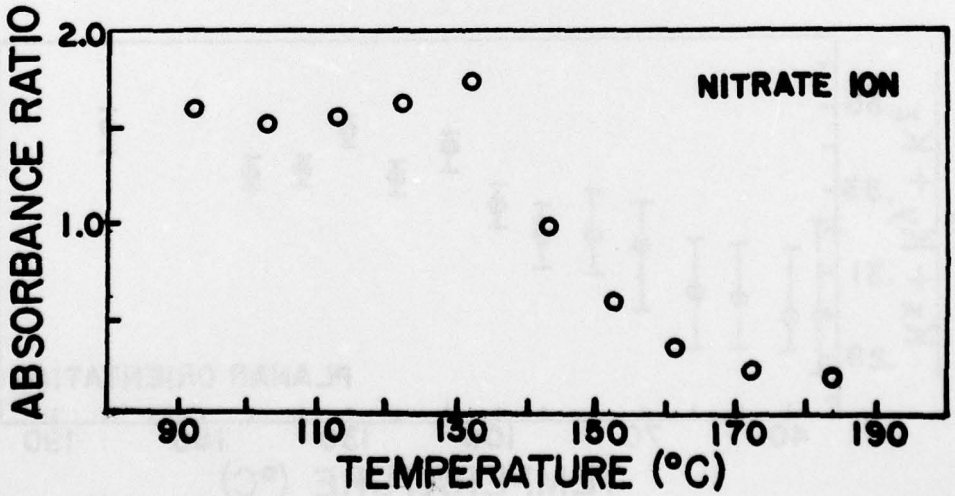
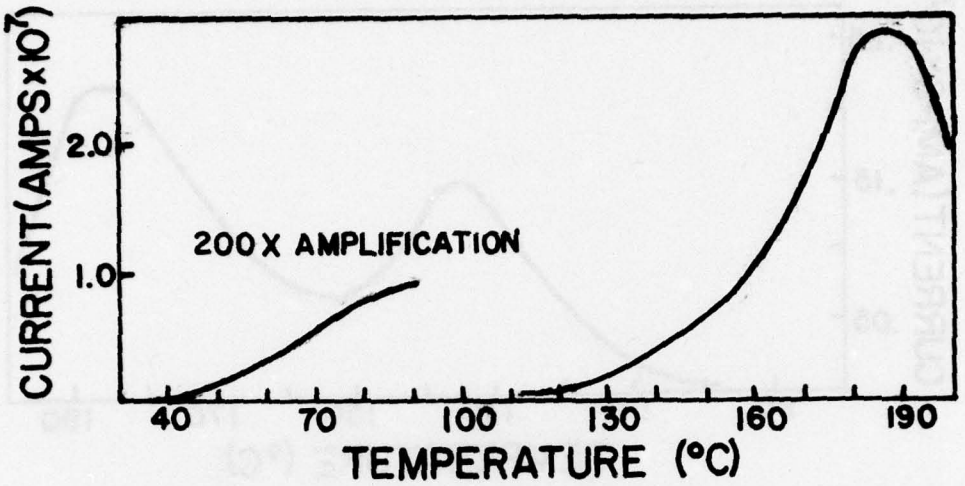
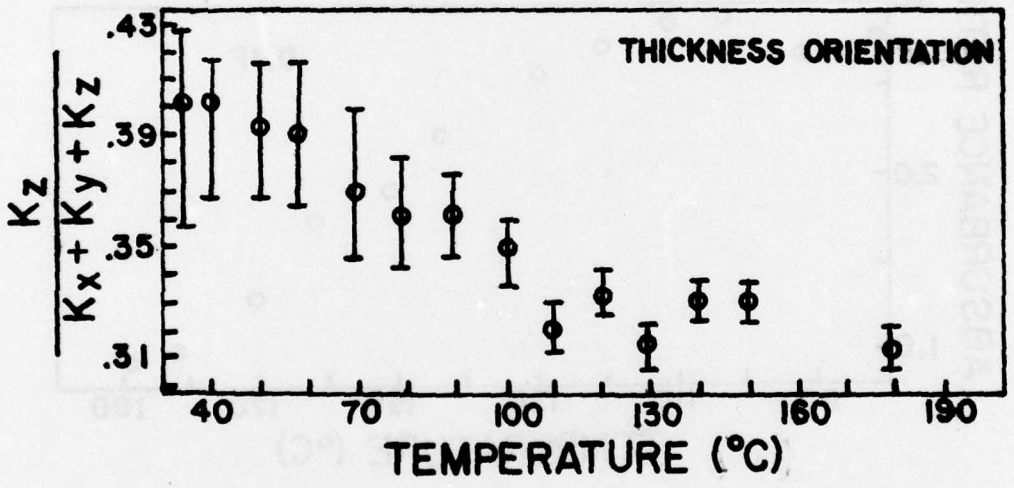

ABSORBANCE RATIO
2.0
1.0
NITRATE ION
90
110
130
150
170
190
TEMPERATURE (°C)

Fig. 2 a,b,c

a)


CURRENT (AMPS x 10⁷)
2.0
1.0
200 X AMPLIFICATION
40
70
100
130
160
190
TEMPERATURE (°C)

b)


Kz / (Kx + Ky + Kz)
.43
.39
.35
.31
THICKNESS ORIENTATION
40
70
100
130
160
190
TEMPERATURE (°C)

c)

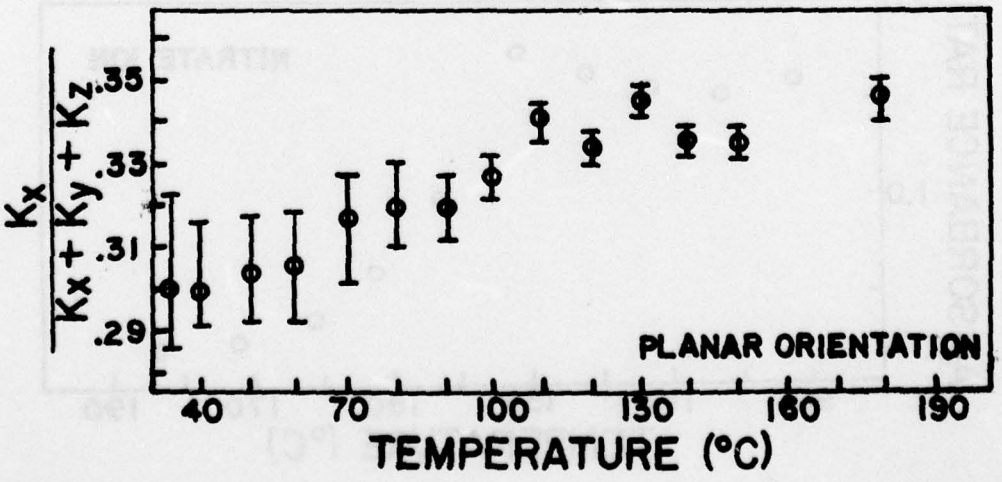
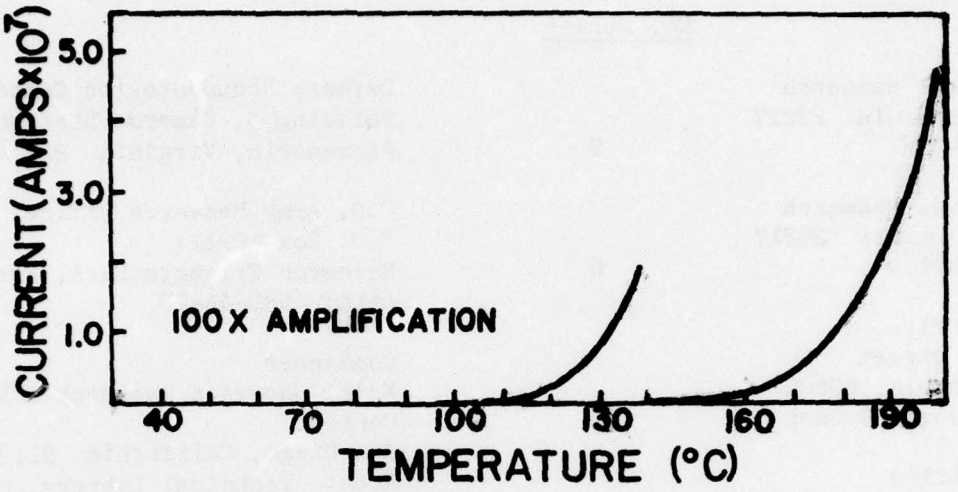
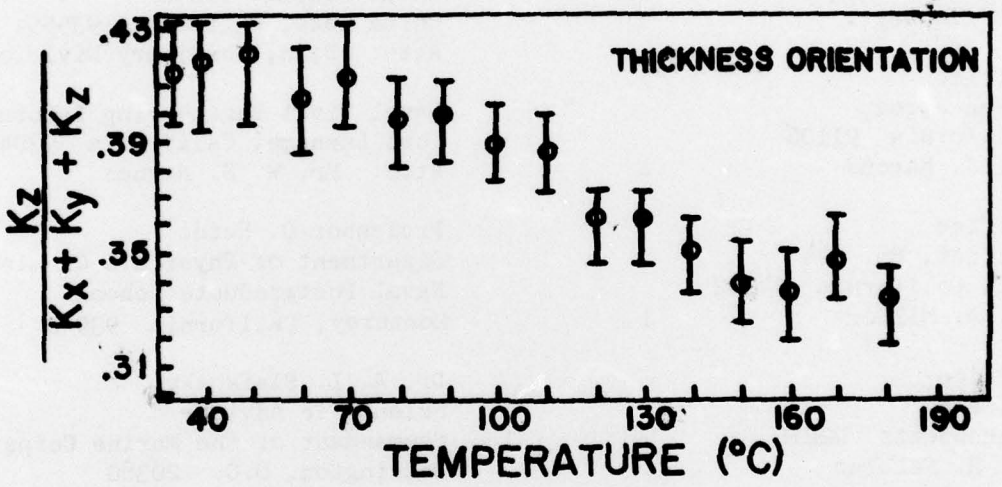

Kx / (Kx + Ky + Kz)
.35
.33
.31
.29
PLANAR ORIENTATION
40
70
100
130
160
190
TEMPERATURE (°C)

Fig. 3 a,b,c

a)


CURRENT (AMPS x 10⁷)
5.0
3.0
1.0
100 X AMPLIFICATION
40
70
100
130
160
190
TEMPERATURE (°C)

b)


Kz / (Kx + Ky + Kz)
.43
.39
.35
.31
THICKNESS ORIENTATION
40
70
100
130
160
190
TEMPERATURE (°C)

c)

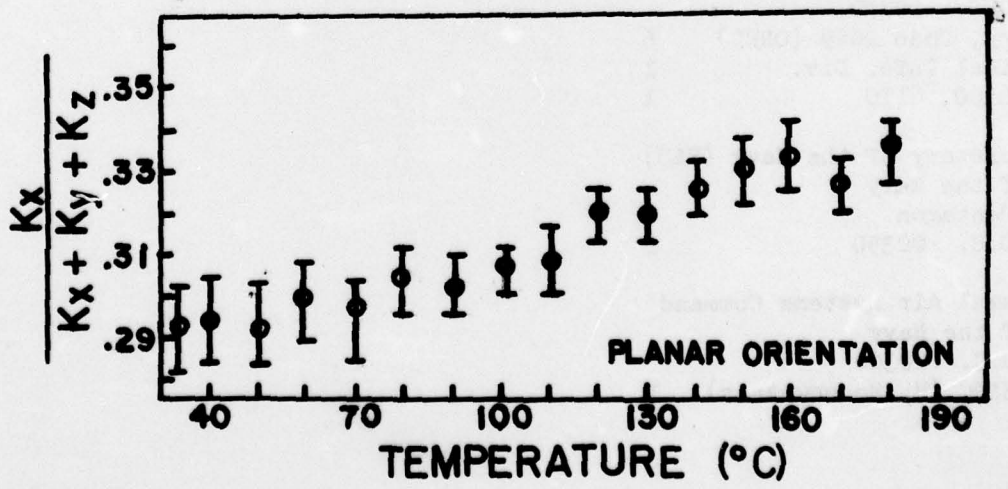

Kx / (Kx + Ky + Kz)
.35
.33
.31
.29
PLANAR ORIENTATION
40
70
100
130
160
190
TEMPERATURE (°C)

Fig. 4 a,b,c

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